

# Pre-formed Cooper pairs and Bose-Einstein condensation in cuprate superconductors

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## Abstract

A two-dimensional (2D) assembly of noninteracting, temperature-dependent, pre-formed Cooper pairs in chemical/thermal equilibrium with unpaired fermions is examined in a binary boson-fermion statistical model as the Bose-Einstein condensation (BEC) singularity temperature  $T_c$  is approached from above. Compared with BCS theory (which is *not* a BEC theory) substantially higher  $T_c$ 's are obtained without any adjustable parameters, that fall roughly within the range of empirical  $T_c$ 's for quasi-2D cuprate superconductors.

A possible interpretation of the “pseudo-gap” observed in some superconductors *above*  $T_c$  is that it arises simultaneously with the formation of “pre-formed” Cooper pairs (CPs). We propose here that such objects emerge naturally as the nonzero-total (or, -center-of-mass) momentum (CMM) CPs that are entirely neglected in ordinary BCS theory.

Consider a 2D system of  $N$  fermions of mass  $m$  confined in a square of area  $L^2$  and interacting pairwise via the BCS model interaction  $V_{\mathbf{k},\mathbf{k}'} = -V$  when  $\mu(T) - \hbar\omega_D < \epsilon_{k_1} (\equiv \hbar^2 k_1^2/2m)$  and  $\epsilon_{k_2} < \mu(T) + \hbar\omega_D$ , and zero otherwise, where  $\mathbf{k} \equiv \frac{1}{2}(\mathbf{k}_1 - \mathbf{k}_2)$  is the relative wavevector of the two particles;  $V_{\mathbf{k},\mathbf{k}'}$  the 2D double Fourier integral of the underlying non-local interaction  $V(\mathbf{r}, \mathbf{r}')$  in the relative coordinate  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ ;  $\mu(T)$  the ideal Fermi gas (IFG) chemical potential

which at  $T = 0$  becomes the Fermi energy  $E_F \equiv \hbar^2 k_F^2/2m$  with  $k_F$  the Fermi wavenumber;  $2\hbar\omega_D \equiv \hbar^2 k_D^2/m$  the energy width of the annulus centered around the Fermi circle and where the interaction is nonzero, with  $\omega_D$  the Debye frequency. For  $V > 0$  this model interaction mimics the net effect of an attractive electron-phonon interaction overwhelming the interfermion Coulomb repulsions.

If  $\hbar\mathbf{K} = \hbar(\mathbf{k}_1 + \mathbf{k}_2)$  is the CMM of a CP, let  $E_K$  be its *total* energy (besides the CP rest-mass energy). The original eigenvalue CP [1] equation for a pair of fermions at  $T = 0$  immersed in a background of  $N - 2$  inert, spectator fermions lying within a (sharp) Fermi circular perimeter of radius  $k_F$ , is then

$$1 = V \sum_{\mathbf{k}}' \frac{\theta(k_1 - k_F) \theta(k_2 - k_F)}{2\epsilon_{\mathbf{k}} + \hbar^2 K^2/4m - E_K}, \quad (1)$$

where  $\theta(x)$  is the Heaviside unit step function, and the prime on the summation sign denotes the conditions  $k_{1,2} \equiv |\frac{1}{2}\mathbf{K} \pm \mathbf{k}| < (k_F^2 + k_D^2)^{1/2}$  ensuring that our pair of fermions *above* the Fermi “surface” cease interacting beyond the annulus of energy width  $2\hbar\omega_D$ , thereby restricting the summation over  $\mathbf{k}$  for a given fixed  $\mathbf{K}$ . Without these restrictions (1) would just be the Schrödinger equation in momentum space for the pair. Setting  $E_K \equiv 2E_F - \Delta_K$ , the pair is *bound* if  $\Delta_K > 0$ , and (1) becomes an eigenvalue equation for the (positive) pair binding energy  $\Delta_K$ . Our  $\Delta_K$  and  $\Delta_0$  should *not* be confused with the BCS energy gap  $\Delta(T)$  at

$T = 0$ . Let  $\lambda \equiv g(E_F)V \geq 0$  be the usual BCS dimensionless coupling constant. Here  $g(E_F)$  is the electronic density-of-states (for each spin) at the Fermi surface in the normal (i.e., interactionless) state, which in 2D is  $g(\epsilon) = L^2 m / 2\pi \hbar^2 \equiv g$ , a constant. The Cooper equation (1) for the unknown quantity  $\Delta_K$  was analyzed in Ref. [2]. For zero CMM,  $K = 0$ , it becomes a single elementary integral, with the familiar [1] solution  $\Delta_0 = 2\hbar\omega_D / (e^{2/\lambda} - 1)$  valid for *all* coupling  $\lambda$ . For small  $K$  one determines [2] for weak coupling,  $\lambda \rightarrow 0$ , that

$$\Delta_K \xrightarrow{K \rightarrow 0} \Delta_0 - \frac{2}{\pi} \hbar v_F K + O(K^2) \quad (2)$$

where  $v_F \equiv \sqrt{2E_F/m}$  is the Fermi velocity. This *linear dispersion relation* is the 2D analog of the 3D result discussed as far back as 1964 in Ref. [3], p. 33 (see also, Ref. [4], p. 336, and [5]) but with the 2D coefficient  $2/\pi$  in (2) replaced by  $1/2$ . Though commonly confused with the Anderson-Bogoliubov-Higgs (ordinary) sound mode, the linear-dispersion result (2) corresponds to real, moving (pre-formed) CPs and is *distinct* from the zero-coupling ABH (indeed, IFG) phonons described by  $\hbar v_F K / \sqrt{3}$ . A general many-body formalism unambiguously exhibiting [6] this distinction involves solving the Bethe-Salpeter equation for Cooper pairing based not on the IFG, as above, but on the BCS ground-state in a Green's functions scheme allowing holes on a par with particles.

For  $N_B$  ordinary bosons of mass  $m_B$  and energy  $\epsilon_K = C_s K^s$  with  $s > 0$  and  $C_s$  a constant, a temperature *singularity* appears at  $T_c \neq 0$  for any [7] dimension  $d > s$  in the number equation  $N_B = \sum_{\mathbf{K}} [e^{(\epsilon_K - \mu_B)/k_B T} - 1]^{-1}$  at vanishing bosonic chemical potential  $\mu_B \leq 0$  when the number of  $\mathbf{K} = 0$  bosons just ceases to be negligible upon cooling. It is given [8] by

$$T_c = \frac{C_s}{k_B} \left[ \frac{s \Gamma(d/2) (2\pi)^d n_B}{2\pi^{d/2} \Gamma(d/s) g_{d/s}(1)} \right]^{s/d} \quad (3)$$

with  $n_B \equiv N_B/L^d$  the boson particle density, and  $g_{d/s}(z)$  the usual Bose integrals expressible as the series

$$g_\sigma(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^\sigma} \xrightarrow{z \rightarrow 1} \zeta(\sigma), \quad (4)$$

where  $\zeta(\sigma)$  the Riemann zeta function of order  $\sigma$ . The last identification in (4) holds when  $\sigma >$

1 for which  $\zeta(\sigma) < \infty$ , while the series  $g_\sigma(1)$  diverges for  $\sigma \leq 1$ , thus giving  $T_c = 0$  for  $d \leq 2$ . For  $s = 2$  and  $d = 3$  one has  $\zeta(3/2) \simeq 2.612$ , and since  $C_2 \equiv \hbar^2/2m_B$  (3) then reduces to the familiar formula  $T_c \simeq 3.31 \hbar^2 n_B^{2/3} / m_B k_B$  of “ordinary” Bose-Einstein condensation (BEC). On the other hand, for either particle or hole bosons with (positive) excitation energy  $\epsilon_K \equiv \Delta_0 - \Delta_K$  given asymptotically by the linear term in (2) for all  $K$ , we have  $C_1 \equiv a(d)\hbar v_F$  where [9]  $a(d) = 1, 2/\pi$  and  $1/2$  for  $d = 1, 2$  and  $3$ , respectively. Now  $T_c$  is *nonzero for all*  $d > 1$ —which is *precisely* the dimensionality range of all known superconductors including the quasi-1D organo-metallic (Bechgaard) salts [10].

The number of bosons in the boson-fermion mixture in chemical/thermal equilibrium turn out [11] to be temperature-dependent, and it is *in conserving the fermion number* that the singularity arises. As in the case of the pure boson gas (3), a linear rather than a quadratic dispersion relation is needed to obtain BEC in *exactly* 2D. All this emerges in a statistical model for the ideal binary gas *mixture* of bosons (the CPs) and unpaired (both pairable and unpairable) fermions in chemical equilibrium [12]. Thermal pair-breaking of the bosons into unpaired pairable fermions is explicitly allowed. At any  $T$  the total number of fermions in 2D is  $N = L^2 k_F^2 / 2\pi = N_1 + N_2$ , and is just the number of non-interacting (i.e., unpairable) fermions  $N_1$  plus the number of pairable ones  $N_2$ . The unpairable fermions obey the usual Fermi-Dirac (FD) distribution with the IFG chemical potential  $\mu$ . On the other hand, the  $N_2$  pairable fermions are simply those in the interaction shell of energy width  $2\hbar\omega_D$  so that

$$N_2 = 2 \int_{\mu - \hbar\omega_D}^{\mu + \hbar\omega_D} d\epsilon \frac{g(\epsilon)}{e^{\beta(\epsilon - \mu)} + 1} = 2g\hbar\omega_D, \quad (5)$$

where  $\beta \equiv (k_B T)^{-1}$ , since a constant  $g(\epsilon)$  renders the remaining integral exact. At any interfermionic coupling and temperature these fermions form an ideal mixture of pairable but unpaired fermions plus CPs that are created near the single-fermion energy  $\mu(T)$ , with binding energy  $\Delta_K(T) \geq 0$  and total energy

$$E_K(T) \equiv 2\mu(T) - \Delta_K(T). \quad (6)$$

This generalizes the  $T = 0$  definition  $E_K \equiv 2E_F - \Delta_K$  given below (1).

The Helmholtz free energy  $F \equiv E - TS$ , where  $E$  is the internal energy and  $S$

the entropy, for this binary gas “*composite boson/pairable-but-unpaired-fermion system*” at  $T \leq T_c$  is then readily constructed [11] in terms of: a)  $n_2(\epsilon)$ , the average number of unpaired but pairable fermions with energy  $\epsilon$ ; b)  $N_{B,0}(T)$ , the number of (bosonic) CPs with zero CMM at temperature  $T$ ; and c)  $N_{B,K}(T)$ , that number of excited pre-formed CPs (i.e., with arbitrary nonzero CMM  $K$ ) and a cutoff  $K_0$  physically defined [2] by  $\Delta_{K_0} \equiv 0$  denoting the value of  $K$  beyond which a CP breaks up. The free energy  $F_2$  of the *pairable* fermions is to be minimized subject to the constraint that  $N_2$  is conserved. If  $N_{20}(T)$  is the number of pairable but unpaired fermions, the relevant *number equation* for the pairable (i.e., active) fermions is then

$$\begin{aligned} N_2 &= N_{20}(T) + 2[N_{B,0}(T) + N_{B,0 < K < K_0}(T)] \\ &\equiv N_{20}(T) + 2N_B(T), \end{aligned} \quad (7)$$

where  $N_{B,0 < K < K_0}(T)$  denotes the *total* number of “excited” bosonic pairs (namely with CMM such that  $0 < K < K_0$ ), i.e.,  $N_{B,0 < K < K_0}(T) \equiv \sum_{0 < K < K_0} N_{B,K}(T)$ . At  $T = 0$  two distinct coupling regimes emerge: a) for  $\Delta_0 < 2\hbar\omega_D$  or for  $\lambda \leq 2/\ln 2 \simeq 2.89$ , we have that  $N_{20}(0) = g(2\hbar\omega_D - \Delta_0)$ ; while b) for  $\Delta_0 > 2\hbar\omega_D$  (or  $\lambda \geq 2.89$ ),  $N_{20}(0)$  is identically zero. Hence, the number of bosons  $N_B(0)$  at  $T = 0$  from (7) is just  $N_B(0) = \frac{1}{2}[N_2 - N_{20}(0)]$ . Using (5) for  $N_2$  the *fractional number of pairable fermions that are actually paired* at  $T = 0$ , namely  $2N_B(0)/N_2 = 1 - N_{20}(0)/N_2$ , becomes simply  $\Delta_0/2\hbar\omega_D = (e^{2/\lambda} - 1)^{-1} \rightarrow e^{-2/\lambda}$  as  $\lambda \rightarrow 0$ , for  $\lambda \leq 2/\ln 2 \simeq 2.89$ , and unity for  $\lambda \geq 2/\ln 2$ . As  $N_B(0) = \frac{1}{2}g\Delta_0$  for  $\lambda \leq 2.89$ , only those fermions in an energy shell of width  $\frac{1}{2}\Delta_0$  around the Fermi surface actually pair at  $T = 0$ , while for  $\lambda \geq 2.89$  *all* pairable fermions pair up since then  $N_B(0) = g\hbar\omega_D \equiv \frac{1}{2}N_2$ . For  $T > 0$ ,  $2N_B(T)/N_2 = 1 - N_{20}(T)/N_2$  decreases with  $T$ , provided one knows  $\Delta_0(T)$  for any  $T \geq 0$  and ascertains that it decreases. For  $T > 0$ , the  $\theta(k_1 - k_F) \equiv \theta(\epsilon_{k_1} - E_F)$  in (1) becomes  $1 - n(\xi_{k_1})$ , where  $n(\xi_{k_1}) \equiv (e^{\beta\xi_{k_1}} + 1)^{-1}$  is the FD distribution with  $\xi_{k_1} \equiv \epsilon_{k_1} - \mu(T)$ , with the IFG chemical potential  $\mu(T)$  in 2D given exactly by  $\mu(T) = \beta^{-1} \ln(e^{\beta E_F} - 1) \rightarrow E_F$  as  $T \rightarrow 0$ . Similarly for  $\theta(k_2 - k_F)$ . Since  $k_1 = k_2$  implies that  $\xi_{k_1} = \xi_{k_2}$ , (1) then leads to a simple generalization to nonzero  $T$  of the  $K = 0$  CP equation,

$$1 = \lambda \int_0^{\hbar\omega_D} d\xi (e^{-\beta\xi} + 1)^{-2} [2\xi + \Delta_0(T)]^{-1}. \quad (8)$$

Numerical solution shows  $\Delta_0(T)$  to indeed be monotonic-decreasing in  $T$  for any fixed  $\lambda$  and  $\hbar\omega_D$ . Further, the solution of  $\Delta_0(T^*) = 0$  is, by inspection,  $T^* = \infty$ ; this infinite “de-pairing” temperature is unrealistic and undoubtedly an artifact of the simplest version (1) of Cooper pairing used here as a starting point; see, however, Ref. [6].

Modeling our system as a *pure boson gas* of CPs (i.e., neglecting the background unpaired fermions) but with a temperature-dependent number density  $n_B(T)$  converts the explicit  $T_c$ -formula (3) into an *implicit* one. For  $s = 1$  and  $d = 2$  it becomes, since  $g_2(1) \equiv \zeta(2) = \pi^2/6$ ,

$$T_c = \frac{4\sqrt{3}}{\pi^{3/2}} \frac{\hbar v_F}{k_B} \sqrt{n_B(T_c)}. \quad (9)$$

This requires  $n_B(T) \equiv N_B(T)/L^2$  which in turn requires  $\Delta_0(T)$  as determined from (8), and follows from the expression  $2N_B(T)/N_2 = 1 - N_{20}(T)/N_2$ . Solving this self-consistently with (7) for  $\lambda = 1/2$  gives the remarkably constant value  $T_c/T_F \simeq 0.004$ , where  $T_F \equiv E_F/k_B$ , over the entire range of  $\nu \equiv \hbar\omega_D/E_F$  values  $0.03 - 0.07$  typical of cuprate superconductors. On the other hand, the BCS formula  $T_c^{BCS} \simeq 1.13\Theta_D e^{-1/\lambda}$  with  $\lambda = 1/2$  gives  $T_c/T_F = 0.005$  to  $0.011$  over the same range of  $\nu$  values. Obviously, both sets of predictions are too small compared with the empirical cuprate range  $T_c/T_F \simeq 0.03 - 0.09$  [13].

The exact  $T_c$  *without* neglecting the background unpaired fermions requires the exact CP excitation energy dispersion relation  $\varepsilon_K(T) \equiv \Delta_0(T) - \Delta_K(T)$  which is neither precisely linear in  $K$  nor independent of  $T$ . To determine  $\Delta_K(T)$  we need a working equation that generalizes Ref. [2] for  $T > 0$  via the new CP eigenvalue equation (8). At  $T = T_c$  both  $N_{B,0}(T_c) \simeq 0$  and  $\mu_B(T_c) \simeq 0$  so that one gets [11] the implicit  $T_c$ -equation for the *binary gas mixture*

$$\begin{aligned} 1 &= \frac{\tilde{T}_c}{\nu} \ln \left[ \frac{1 + e^{-\{\tilde{\Delta}_0(\tilde{T}_c)/2 - \nu\}/\tilde{T}_c}}{1 + e^{-\{\tilde{\Delta}_0(\tilde{T}_c)/2 + \nu\}/\tilde{T}_c}} \right] + \frac{8(1 + \nu)}{\nu} \\ &\times \int_0^{\kappa_0(\tilde{T}_c)} d\kappa \frac{\kappa}{e^{[\tilde{\Delta}_0(\tilde{T}_c) - \tilde{\Delta}_\kappa(\tilde{T}_c)]/\tilde{T}_c} - 1}, \end{aligned} \quad (10)$$

where quantities with tildes are in units of  $E_F$  or  $T_F$ ;  $\kappa \equiv K/2(k_F^2 + k_D^2)^{1/2}$  with  $k_D$  defined through  $\hbar\omega_D \equiv \hbar^2 k_D^2/2m$ ; and  $\nu \equiv \Theta_D/T_F$ . To obtain  $T_c$  from the finite- $T$  dispersion relation one must numerically solve *four* equations self-consistently for each  $\lambda$  and  $\nu$ , namely (10) in

conjunction with (8) for  $\tilde{\Delta}_0(\tilde{T})$ , and Eq. (35) of Ref. [2] for both  $\tilde{\Delta}_\kappa(\tilde{T})$  and the breakup value  $\kappa_0(\tilde{T}_c)$ . For  $\lambda = 1/2$  and the range of  $\nu$  values 0.03 – 0.07 typical of cuprates, the resulting  $T_c/T_F$  falls within the aforementioned empirical range 0.03 – 0.09 [13]. For cuprates  $d \simeq 2.03$  has been suggested [14] as more realistic since it reflects inter-CuO-layer couplings, but our results in that case would be very close to those for  $d = 2$  since, e.g., from (3)  $T_c$  for  $s = 1$  (but *not* for 2) varies little with  $d$  around  $d = 2$ . In fact, if  $m_{B\perp}$  and  $m_B$  are the boson masses *perpendicular* and *parallel*, respectively, to the cuprate planes, an “anisotropy ratio”  $m_B/m_{B\perp}$  varied from 0 to 1 allows “tuning”  $d$  continuously from 2 to 3.

Other boson-fermion models [15][16][17][18][19] have been introduced, some even addressing [17][18]  $d$ -wave interaction effects as opposed to the pure  $s$ -wave considered here, and some also focus [18][19] on the pseudogap. But calculating cuprate  $T_c$  values in quasi-2D without adjustable parameters has not been attempted, and indeed  $T_c \equiv 0$  is predicted in exactly 2D.

In summary, a simple statistical model treating pre-formed CPs with *both* zero and nonzero CMM as non-interacting bosons in chemical/thermal equilibrium with unpaired fermions is proposed that gives rise to a boson number that is strongly coupling- and temperature-dependent. Since the CP dispersion relation is approximately linear for nonzero CMM, it exhibits a BEC of zero-CMM pairs at precisely 2D. In contrast to both BCS theory—which is *not* [20] a BEC theory—and simpler BE models excluding either the breakable character of the pre-formed CPs or the presence of unpaired fermions, exact  $T_c$ ’s for the boson-fermion binary mixture based upon the *exact* CP dispersion relation are found in rough agreement with empirical cuprate values with no adjustable parameters.

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